NSWC TR 84-388

KINETICS AND MECHANISM FOR THE BASIC HYDROLYSIS OF BIS (2,2-DINITROPROPYL) ACETAL (BDNPA) AND BIS (2,2-DINITROPROPYL) FORMAL (BDNPF)

BY   JOHN C. HOFFSOMMER
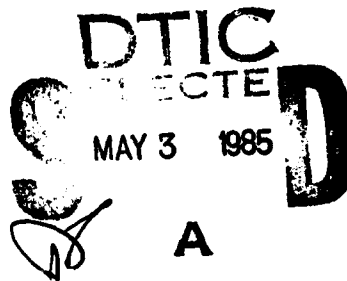
RESEARCH AND TECHNOLOGY DEPARTMENT

1 MARCH 1985

DTIC
ECTE
MAY 3 1985
A

NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 ● Silver Spring, Maryland 20910

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC TR 84-388	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) KINETICS AND MECHANISM FOR THE BASIC HYDROLYSIS OF BIS (2,2-DINITROPROPYL) ACETAL (BDNPA) AND BIS (2,2-DINITROPROPYL) FORMAL (BDNPF)		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John C. Hoffsommer		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center (Code R16) White Oak, Silver Spring, Maryland 20910		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62765N, F65559, SF65559691; R18BA(4)
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Sea Systems Command (SEA-62R32) Washington, DC 20362		12. REPORT DATE 1 March 1985
		13. NUMBER OF PAGES 37
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Bis (2,2-dinitropropyl) acetal (BDNPA)
Bis (2,2-dinitropropyl) formal (BDNPF)
Hydrolysis
Kinetics
Explosives

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The kinetics for the alkaline homogeneous hydrolysis of bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF) in water and 53% dioxane-water with sodium hydroxide concentrations between 0.14 and 1.9 molar and temperatures between 40° and 70°C have been investigated. Both BDNPA and BDNPF were found to react with slightly more than four moles of base to yield nitrite, 1,1-dinitroethane, acetate and formate anions. Good second order rate constants were obtained for both BDNPA and BDNPF for the expression

20. (Continued)

-d(BDNPA/dt = k_1(BDNPA) = k_2(B_u^-)(BDNPA), were k_1 is the first order rate constant with excess base, B_u^-, BDNPA and BDNPF were found to react faster in dioxane-water than in water. The rates of disappearance of both BDNPA and BDNPF were very nearly equal to one half the combined rates for the formation of nitrite and 1,1-dinitroethane anions, and suggest concurrent competing E-2 elimination (78 ± 5%) and SN-2 nucleophilic displacement (20 ± 3%) reactions with base. On the basis of relative K_2 values, BDNPA and BDNPF were found to react forty times faster with aqueous base than triethyleneglycol dinitrate (TEGDN), but one thousand times slower than 1,3,5-triaza-1-3,5-trinitro-cyclohexane (RDX). The kinetics of the alkaline hydrolysis of BDNPA and BDNPF are discussed in terms of the products formed, and mechanisms are suggested for the formation of these products.

+ or -

EXECUTIVE SUMMARY

The kinetics for the alkaline homogeneous hydrolysis of bis(2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF) in water and 53 percent dioxane-water with sodium hydroxide concentrations between 0.14 and 1.9 molar and temperatures between 40° and 70° have been investigated. Both BDNPA and BDNPF were found to react with slightly more than four moles of base to yield nitrite, 1,1-dinitroethane, acetate, and formate anions. Good second order rate constants were obtained for both BDNPA and BDNPF for the expression, $-d(BDNPA)/dt = k_1(BDNPA) = k_2(B^-)(BDNPA)$, where k is the first order rate constant with excess base, B^-. BDNPA and BDNPF were found to react faster in dioxane-water solutions than in water. The rates of disappearance of both BDNPA and BDNPF were very nearly equal to one half the combined rates for the formation of nitrite and 1,1-dinitroethane anions, and suggest concurrent competing E-2 elimination (78 ± 5 percent) and Sn-2 nucleophilic displacement (20 ± 3 percent) reactions with base. On the basis of relative k_2 values, BDNPA and BDNPF were found to react forty times faster with aqueous base than triethylene glycol dinitrate (TEGDN), but one thousand times slower than 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX). The kinetics of the alkaline hydrolyses of BDNPA and BDNPF are discussed in terms of the products formed, and mechanisms are suggested for the formation of these products.

FOREWORD

This work was supported by the Naval Sea Systems Command (SEA 62R), Washington, D.C. 20362, under the title: "Pollution Potential of Explosives in Water;" on Task No. SF 65559691 as part of the Ordnance Pollution Abatement Block Program.

Since the loading and reclamation of Navy PBX ingredients often involve large quantities of water which can become contaminated, it is essential that reliable methods be available to measure the extent of this contamination so that clean up procedures can be initiated. Adsorptive, hydrolytic, and photolytic methods are being investigated in order to assess their potential as means to remove these contaminants efficiently and with no adverse effect on the environment. This report describes the alkaline hydrolysis of bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BNDPF).

Approved by:

J. F. PROCTOR, Head
Energetic Materials Division

CONTENTS

ILLUSTRATIONS

TABLES

INTRODUCTION

During the loading or reclamation of Naval ordnance, large volumes of water often become contaminated with in-service energetic materials. In order to assess the extent of this contamination and to monitor the efficiency of any clean-up procedure employed, it is essential that reliable methods be available for the detection and analysis of the specific materials involved. For hydrolytic [1,2,3] photolytic[4,5] or microbiological[6,7] procedures which involve chemical changes, it is extremely important that the chemistry be understood as much as possible, and that the respective transformation products be identified so that reasonable procedural choices may be made. Ideally, these transformation products should not produce any adverse effects on the environment. This report describes the kinetics and mechanisms for the basic hydrolysis of bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF).

EXPERIMENTAL

MATERIALS

Bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal

1. Hoffsommer, J.C., Glover, D.J. and Burlinson, N.E., "Kinetics and Mechanism for the Alkaline Homogeneous Hydrolysis of 1,1,1-Trimethylolethane Trinitrate (MTN)," J. Org. Chem., Vol 48, 1983, pp. 315-321.
2. Hoffsommer, J.C., Kinetics and Mechanism for the Alkaline Homogeneous Hydrolysis of Triethyleneglycol Dinitrate (TEGDN), NSWC TR 83-110, 23 May 1983.
3. Hoffsommer, J.C., Kubose, D.A., and Glover, D.J., "Kinetic Isotope Effects and Intermediate Formation for the Aqueous Alkaline Homogeneous Hydrolysis of 1,3,5-Triaza-1,3,5-trinitrocyclohexane (RDX)," J. Phys. Chem., Vol 81, 1977, pp. 380-385.
4. Glover, D.J., Photolysis of Metriol Trinitrate II, Ultraviolet Radiation Plus Ozone, NSWC TR 82-428, 1 Aug 1982.
5. Glover, D.J. and Hoffsommer, J.C., Photolysis of RDX. Identification and Reaction of Products, NSWC TR 79-349, 1 Dec 1979.
6. Hoffsommer, J.C., Kaplan, L.A., Glover, D.J., Kubose, D.A.,Dickinson, C., Goya, H., Kayser, E.G., Groves, C.L., and Sitzman, M.E., Biodegradability of TNT: A Three Year Pilot Study, NSWC TR 77-136, 13 Feb 1978.
7. McCormick, N.G., Cornell, J.H.,and Kaplan, A.M., "Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX)," Applied and Environmental Microbiology, Vol 42, No. 5, 1981, pp. 817-823.

(BDNPF) were prepared and purified from 2,2-dinitropropanol and acetaldehyde or formaldehyde in sulfuric acid according to the procedure of Shipp and Hill.[8] 2-Nitro-1-propanol (Aldrich Chemical Company) was checked for purity by liquid chromatography (LC). Formic acid (Eastman Organic Chemicals) was determined to be 98.2% pure by acid titration. Glacial acetic acid and sodium nitrite were obtained commercially as analytical reagents, and together with formic acid were used as ion chromatographic (IC) standards. Distilled water and ' LC grade organic solvents were used in all experiments.

ANALYSES

Concentrations of bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF) were determined with a liquid chromatograph (Hewlett-Packard, Model 1084A), equipped with a variable wavelength detector (HP Model 1030) and a variable injector using a 10 micrometer RP-8 column, 25 cm X 4.6 mm ID at 40°C; eluent, 53% methanol/water (v/v); flow, 2.5 ml/min.; detector wavelength, 220 nm; attenuation, 0.0064 AU/cm. Under these conditions, a 100 microliter injection of 8.60×10^{-5} M BDNPF gave a peak height of 107.8 mm with a retention time of 4.0 minutes, while a 100 micro liter injection of 8.32×10^{-5} M BDNPA gave a peak height of 83.1 mm with a retention time of 5.1 minutes.

In some cases, due to the low solubility of BDNPA and BDNPF in water (approximately 4.7×10^{-5} M at room temperature), analyses were conducted by gas chromatography (GC) employing the nickel-63 electron capture (ec) detector.[9] A research gas chromatograph, HP model 5754, equipped with a Model 5763A nickel-63 electron capture (ec) detector and a Model 7128A Mosely dual channel recorder was used for the analyses of BDNPA in water under the following conditions: 4 ft X 1/4 in. glass column, packed with 3.52% Dexsil 300 GC on 80/100 high performance chromosorb W (Varian Associates); column, 175°C; injector, 185°C; 209 ml/min, argon/methane, 95/5 (v/v); Ni-63 ec

8. Shipp, K.G., and Hill, M.E., "Acetal Preparation in Sulfuric Acid," J. Org. Chem., Vol 31, 1956, p. 835.
9. Hoffsommer, J.C., Kubose, D.A., and Glover, D.J., Microanalysis of Selected Energetic Nitro Compounds by Gas/Liquid Chromatography (GC/LC), NSWC TR 80-535, 14 Jan 1981.

detector, 285°C; attenuation, 10 X 80. Under these conditions a 1.0 microliter injection of 6.37 X 10^{-6} M BDNPA and 1.69 X 10^{-6} M TNT (as internal standard) in pesticide grade benzene (Fisher Scientific Company) gave the following peak heights and retention times: 145.5 mm, 1.57 min. (TNT); and. 126 mm, 4.64 min. (BDNPA).

Peak heights at the respective retention times for both the LC and GC analysis of BDNPA and BDNPF were used to calculate unknown concentrations by comparison to standards of BDNPA and BDNPF of known concentrations. Precision of repeated injections was usually better than ± 3%.

Nitrite ion concentrations were measured with an ion chromatograph (Dionex Model 10) using a 3 mm by 500 mm anion separator column with a 3 mm by 150 mm pre-column, and a 6 mm by 250 mm anion suppressor column; eluent, 0.003 M sodium bicarbonate and 0.0024 M sodium carbonate in distilled water; flow rate, 2.3 ml/min.; sensitivity, 3 micromhos, full scale. Typically, under these conditions, a 100 microliter injector of a 4.33 X 10^{-4} M aqueous nitrite ion solution gave a peak height of 175 mm with a retention time of 5.4 minutes.

Formate and acetate ion concentrations were ascertained by using a 0.005 M borax solution in water as eluent under the conditions outlined for the nitrite ion analysis. Typically, a 100 microliter injection of a mixture of 3.49 X 10^{-4} M acetate ion and 5.3 X 10^{-4} M formate ion gave the following peak heights and retention times: 54.0 mm, 4.5 min. (acetate ion); and, 115.2 mm, 6.5 min. (formate ion).

For quantative measurements the peak heights of nitrite, formate and acetate ions were compared to those of standard solutions. Precision of repeated injections was usually better than ± 3%.

Concentrations of 1,1-dinitroethane anion were monitored spectrometrically[10] at 380 nm where the 1,1-dinitroethane anion is reported to have a molar absorbancy of 16,880.

---

10. Glover, D.J., "Spectrophotometric Method for the Quantitative Analysis of Trinitromethyl Compounds," Tetrahedron, Vol 19, Suppl. 1, 1963, pp. 219-233.

KINETICS

Stock aqueous or dioxane/water [53/47 (v/v)] solutions of BDNPA or BDNPF and sodium hydroxide were thermostated separately in 10 ml volumetric flasks in a constant temperature bath held to $\pm$ 0.05°C at least one-half hour before a run. Concentrations of stock solutions were chosen so that on mixing the final base concentration was at least fifty times the BDNPA or BDNPF concentration. Appropriate aliquots were taken periodically by means of a micropipet and added to a known volume of distilled water, resulting in concentrations of BDNPA or BDNPF between 10^{-4} and 10^{-5} M. Base concentrations were determined at the conclusion of a run by standard acid titration of an aliquot of the reaction solution. Ion chromatographic (IC) analyses for nitrite, acetate and formate anions were carried out directly on the diluted aqueous samples as were the spectrophotometric determinations of 1,1-dinitroethane anion. Liquid chromatographic (LC) analyses were conducted on a one to two millimeter portion of the diluted sample after adjusting the pH to 7-8 by the addition of small portions of solid potassium dihydrogen phosphate. Whenever gas chromatography (GC) was used to analyze BDNPA, appropriate aliquots of the reaction mixture at various times were added to 4.0 millimeters of 0.1 M aqueous potassium dihydrogen phosphate, followed by extraction with 4.0, 3.0, or 2.0 milliliters of benzene (depending on the extent of the reaction) containing TNT as an internal standard.

RESULTS AND DISCUSSION

The alkaline hydrolyses of both BDNPA and BDNPF were found to be complex and involved a number of bond-scissions. The products formed (Table 1) were nitrite, 1,1-dinitroethane, acetate and formate anions; while, in addition, a trace of 2-nitro-1-propanol was detected among the BDNPF hydrolysis products. The formation of these products involved cleavage of carbon-nitrogen, as well as carbon-oxygen bonds. The formation of nitrite anion accounted for about 50% of the available nitrogen present for both BDNPA and BDNPF (Tables 2 and 3) while, 1,1-dinitroethane anion represented only about 25% of the available nitrogen. Together, these two products comprised about 75% of the available nitrogen and left 25% among the hydrolysis products.

The formation of acetate and formate anions (Table 1) for both BDNPA and BDNPF showed disruption of the acetal and formal carbon-oxygen bonds.

4

Regression of BDNPA or BDNPF formation,[8,11] would be expected to produce two moles of 1,1-dinitroethane anion, two moles of formaldehyde, and one mole of acetaldehyde from BDNPA, but two moles of 1,1-dinitroethane anion, and three moles of formaldehyde from BDNPF. That this was not the case is seen in Table 1, where only 19.5% of the theoretical 1,1-dinitroethane anion was formed from BDNPA hydrolysis (19.5% = (12.7)/(2)(32.6) X 100), and 25% of the theoretical 1,1-dinitroethane anion was formed from BDNPF (25.0% = (18.4/(2)(36.7) X 100). In addition, no formaldehyde was detected among the hydrolysis products of either BDNPA or BDNPF by the chromatropic acid test.[12] Furthermore, the absence of methanol among the reaction products, as shown by gas chromatographic analysis, precludes a Cannizzaro-type reaction with formaldehyde and base.[13]

Although both acetate (CH_3COO^-) and formate ($HCOO^-$) ions might be expected to result from BDNPA hydrolysis, it is somewhat suprising that the acetate ion concentration (Table 1) was almost twice the formate ion concentration. These results indicate carbon-carbon bond cleavage in the 2,2-dinitropropyl group. Support for this theory is the formation of acetate ion in the hydrolysis of BDNPF although in a smaller yield than observed for BDNPA. The total carbon found among the products identified was 32.4% from BDNPA hydrolysis and 37.6% from BDNPF hydrolysis.

Both BDNPA and BDNPF consumed approximately four moles of base for each mole hydrolyzed, Table 1. The fact that each mole of BDNPA and BDNPF contains four nitro groups, and that nearly four moles of base were consumed for each mole reacted may be somewhat fortuitous since only about 75% of the theoretical nitro groups were accounted for among the products listed in Tables 1, 2, and 3. However, the molar yields of NO_2^- and $CH_3C(NO_2)_2^-$,

8. Shipp, K.G. and Hill, M.E., "Acetal Preparation in Sulfuric Acid," _J. Org. Chem._, Vol 31, 1956, p.835.

11. Hall, T.N., "Reactions of Nitro Alcohols II. The Kinetics of Dissociation of 2,2-Dinitropropanol in Aqueous Buffers," _J. Org. Chem._, Vol 30, 1965, p. 3157.

12. Eegriwe, E., _Z. Anal. Chem._, Vol 110, 1937, p. 22 (with modifications by Cares, J.W., _Amer. Ind. Hyg. Assoc._ Vol 29, 1968, p. 405).

13. Beringer, F. M., Ed. _Formaldehyde_ (New York: Reinhold, 1964), p. 214 (reporting work of Fry, H. S., Uber, J. J., and Price, J. W., _Recl. Trav. Chim Pays-Bas._, Vol. 50 1931, pp 1060-1065).

(Tables 2 and 3) were found to be fairly independent of solvent and base strength, and indicate similar concurrent competing reactions.

Rate constants for the alkaline hydrolysis of BDNPA or BDNPF are given in Table 4. Where the NaOH concentration was at least fifty times the BDNPA or BDNPF concentration, pseudo first order rate constants, k_1, were calculated from the expression, $k_1 = t^{-1}\ln(C_0/C_t)$, where t is the time in seconds, and C_0 and C_t represent the initial concentrations of BDNPA or BDNPF and the concentrations at the time, t. Values of k_1 were obtained from the slopes of $\ell n \, C_t$ versus time plots. Linear regression equations for the specific data points were generated by a least squares method which gave the error in k_1 and the correlation coefficient to a straight line fit. At the 95% confidence level, the correlation coefficients were better than 0.99 for the number of data points listed. A typical plot is shown in Figure 1. Second order rate constants, k_2, listed in Table 4, were calculated from k_1 by the expression, $k_2 = k_1/(\text{NaOH})$. Since the NaOH concentrations were determined by acid titration and are more accurate than the k_1 values, the errors listed for the k_2 values reflect errors in k_1. The relationships of k_1 and k_2 to the rate expressions for the disappearance of BDNPA or BDNPF are shown in equations (1) through (4) and illustrated for BDNPA.

(1)　　　$-d(\text{BDNPA})/dt = k_2(\text{NaOH})^x(\text{BDNPA})^y$ (rate expression for disappearance of of BDNPA)

(2)　　　$(\text{NaOH}) \gg (\text{BDNPA})$ (concentration of NaOH much greater than concentration of BDNPA)

(3)　　　$k_1 = k_2(\text{NaOH})^x = t^{-1}\ln(\text{BDNPA})_0^y/(\text{BDNPA})_t^y = t^{-1}\ln(\text{BDNPA})_0/(\text{BDNPA})_t$ (psudo first order rate expression for disappearance of BDNPA)

(4)　　　$k_2 = k_1/(\text{NaOH})^x$ (relationship between first and second order rate constants)

According to equation (4), if $x = 1$, then k_1 should vary linearly with sodium hydroxide concentration, since k_2 is constant. In this case, the order with respect to the sodium hydroxide concentrations would be one. That this was the case is shown for runs 4 and 5 for BDNPA, as well as for runs 12, 13, and 14 for BDNPF (Table 4).

At a given temperature, both BDNPA and BDNPF were found to hydrolyze much faster in dioxane-water than in water alone. For example, at 70°C (runs 5 and

6, Table 4) BDNPF was found to hydrolyze 9.1 times faster (62.1/6.8 = 9.1) in dioxane-water than in water alone. The same was true for BDNPF at 70°C (comparing runs 12, 13, and 14 with runs 15, and 16, Table 4), but in this case BDNPF was found to hydrolyze only 3.1 times faster (31/10 = 3.1) in dioxane-water than in water alone.

A reasonable explanation for the hydrolysis rate differences between BDNPA and PDNPF in dioxane-water can be made based on the activation parameters for BDNPA and BDNPF in water (Table 7). The heats of activation, $\Delta H^{\neq}$ are different for BDNPA (23.9 kcal/mole) and BDNPF (27.3 kcal/mole), while the free energy of activation, $\Delta H^{\neq}$(25.1 kcal/mole) for both BDNPA and BDNPF are practically the same.

Since $\Delta F^{\neq}$ is directly proportional to the rate of reaction by the expression, $\Delta F^{\neq} = -RT \ell n \, (k_2 h)/(kT)$, where h is Planck's constant, and k is Boltzmann's constant; the changes in $\Delta F^{\neq}$ are directly proportional only to the changes in the entropy of activation, $\Delta S^{\neq}$, where $\delta \Delta F^{\neq}$ is zero. Under these conditions, an isokinetic (where rates of reaction are equal) relationship exists and may be expressed in equation (5).[14]

$$(5) \qquad \delta \Delta H^{\neq} = \beta \delta \Delta^{\neq}$$

From the data in Table 7, the isokinetic temperature, β, for BDNPA and BDNPF in water was calculated to be 324°K (or 51°C) which is close to 55°C where the hydrolysis rates of BDNPA and BDNPF were observed to be practically the same (Table 4, runs 3 and 8). However, at temperatures higher than the isokinetic temperature, e.g., at 70°C, BDNPF was found to react about 1.5 times faster (10/6.8 = 1.5) than BNDPA. Conversely, at temperatures lower than the isokinetic temperature, BDNPF would be expected to hydrolyze slower than BDNPA.

A similar situation must exist for the activation parameters for BDNPA and BDNPF in dioxane-water. Although those for BDNPA were not measured in dioxane-water, a reasonable estimate of $\Delta H^{\neq}$ for BDNPA may be made by comparison with the changes in $\Delta H^{\neq}$ for BDNPF from the solvent water to dioxane-water. Assuming that a 4.5 kcal/mole decrease in $\Delta H^{\neq}$ is the same for BDNPA as for BDNPF in changing from water to dioxane-water (i.e., $\Delta H^{\neq}$ for BDNPA is 19.5

---

14. Leffler, J. F., J. Org. Chem., Vol. 20, 1955, p 1202

(Kcal/mole), and using the second order rate constant, K_2, for the hydrolysis of BDNPA in dioxane-water at 70°C (Table 4, run 6), a value of -12 cal/deg for the entropy of activation for BDNPA in dioxane-water may be calculated from the expression in equation (6). The $\Delta S^{\neq}$ estimated for BDNPA in dioxane-water

$$(6) \quad \Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} = -RT\ln(k_2 h/kt)$$

is as expected on comparison with the $\Delta S^{\neq}$ of BDNPF which becomes 10.9 cal/deg more negative in dioxane-water than in water. In general, decreases in entropies of activation, $\Delta S^{\neq}$, can be expected for reactions in less polar solvents (dioxane-water) relative to the entropies found for the same reaction in polar solvents (water).[15]

On the basis of the similar product mole ratios of NO_2^- and $CH_3(NO_2)_2^-$ for BDNPA and BDNPF (Tables 2 and 3), there is no reason to suspect a change in mechanism from BDNPA to BDNPF even though in water there is a 3.4 kcal/mole difference in the activation energy, $\Delta H^{\neq}$, Table 7. Indeed, as has been pointed out,[16] reactions having the same mechanism can often differ by activation energies of 5 kcal/mole or more. Plots of $\ln k_2$ versus $1/T$ for BDNPF in water and dioxane-water are shown in Figure 4. Slopes of these lines were used to calculate $\Delta H^{\neq}$ from the expression, $\Delta H^{\neq} = $ (slope)(R)- RT. Correlation coefficients were better than 0.99 for the linear regression equation fit by a least squares method.

Tables 5 and 6 show the kinetic data obtained for the disappearance of BDNPA and BDNPF, respectively, together with the formation of nitrite and 1,1-dinitroethane anions. Initial rates of disappearance of BDNPA,[-d(BDNPA)/dt], and the rates of formation of nitrite ion, [+d(NO_2^-)/dt], and 1,1-dinitro-ethane ion, [+d($CH_3C(NO_2)_2^-$)/dt], calculated for the first 5 minutes were found to be 0.192 X 10^{-3} M/min.,0.32 X 10^{-3} M/min. and 0.068 X 10^{-3} M/min. respectively. Since BDNPA contains two dinitropropyl groups, a statistical correction of 1/2 needs to be applied to the rates of formation of nitrite and 1,1-dinitroethane anions. These results are shown in equation 7.

15. Gould, E. S., Mechanism and Structure in Organic Chemistry, (New York: Holt, Rinehart and Winston), 1959, p. 182.
16. Leffler, J. E., and Grunwald, E., Rates and Equilibrium of Organic Reactions, (New York: John Wiley and Sons), 1963, p. 326.

(7) $-d(BDNPA)/dt = 1/2\ (+d(NO_2^-)/dt + \ +d(CH_3C(NO_2^-)_2/dt)$

       0.192   0.32   0.068   rates M X 10^{-3}/min.

In a similar manner, the initial rates for the disappearance of BDNPF, calculated for the first 5 minutes were found to be approximately equal to 1/2 the combined rates for the formation of nitrite and 1,1-dinitroethane anions. These results are shown in equation 8.

(8) $-d(BDNPF)/DT = 1/2\ (+\ d(NO_2^-)/dt + \ +d(CH_2C(NO_2^-)_2)$

       0.194   0.282   0.090   rates, M X 10^{-3}/min

The most probable mechanism for the base hydrolysis of both BDNPA and BDNPF involves two concurrent competing reactions, namely: (1) a concerted E-2 type elimination to form NO_2^- ion, involving a slow proton abstraction from the methylene carbon between the gem-dinitro group and the formal (BDNPF) or acetal (BDNPA) oxygen, followed by a rapid elimination of NO_2^- ion, and, (2) a slow SN-2 nucleophilic displacement on the same methylene carbon to form the 1,1-dinitroethane anion. A schematic for these reactions is shown for BDNPF, $(CH_3C(NO_2)_2CH_2O)_2CH_2$, although the same would hold true for BDNPA, $(CH_3C(NO_2)_2CH_2O)_2CHCH_3$.

BDNPF

$$(CH_3C(NO_2)_2CH_2O)_2CH_2$$

E-2   SN-2

$-H_2O$, slow   slow

$$(CH_3C(NO_2)_2CHO)_2CH_2$$

| fast

$$(CH_3C(NO_2)=CHO)_2CH_2 \qquad\qquad (HOCH_2O)_2CH_2$$

not isolated   not isolated

unidentified products

+

$$NO_2^- \quad + \quad HCOO^- \quad + \quad CH_3COO^- \quad + \quad CH_3C(NO_2)_2^-$$

identified products
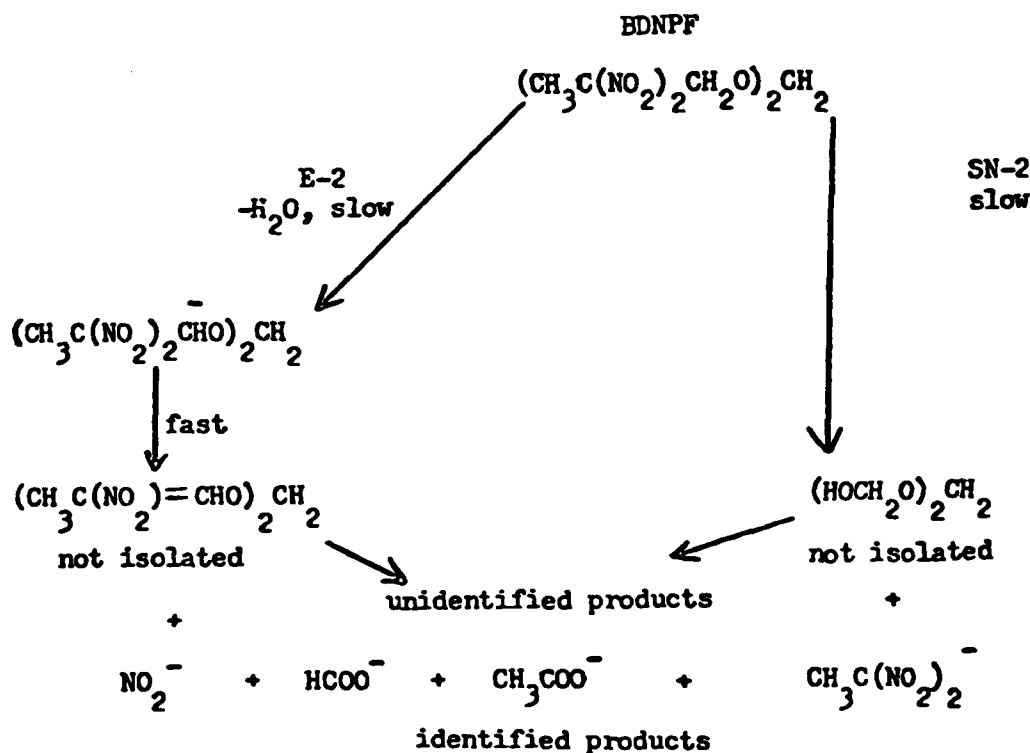
Schematic for the Alkaline Hydrolysis of BDNPF

Since $[d(NO_2^-)/dt]/[d(CH_3)C(NO_2^-)_2/dt] = (NO_2^-)/(CH_3)C(NO_2^-)_2$, the ratios of nitrite anion to 1,1-dinitroethane anion listed in Tables 5 and 6 should be proportional to the ratios of the initial rates found in equations 7 and 8. The ratio found for BDNPA, equation 7, was 4.7 (equal to 0.32/0.068) while the ratio found for BDNPF, equation 8, was 3.1 (equal to 0.282/0.090). These values are close to the individual mole ratios, $NO_2^-/CH_3C(NO_2^-)_2$, for both BDNPA (Table 5) and BDNPF (Table 6). From these data, it can be seen that the E-2 elimination reaction for both BDNPA and BDNPF is about four times more rapid than the SN-2 nucleophilic reaction. The somewhat lower yield of 1,1-dinitroethane anion for BDNPA (19%) than for BDNPF (25%) indicates that the SN-2 reaction is slightly less important in the case of BDNPA.

Finally, it is of some interest to compare the second order rate constants, k_2, obtained for the alkaline hydrolyses of several classes of nitro compounds listed in Table 8. From these rates the following order of decreasing stability towards base can be established:

TEGDN (most stable)>MTN>>BDNPA $\cong$ BDNPF>>> RDX (least stable).

The rate data given in Table 4 together with the activation parameters listed in Table 7 are useful in making predictions of the half-lives of BDNPA and BDNPF in water for any base strength desired. At 25°C, the second order rate constants, k_2, for BDNPA and BDNPF were calculated to be 3.31×10^{-6} Lmole^{-1}sec^{-1} and 2.04×10^{-6} Lmole^{-1}sec^{-1}, respectively. From these values and using equations 3 and 4 at pH 7, the half-lives of BDNPA and BDNPF would be expected to be 6.6×10^4 years and 10.7×10^4 years, respectively. In 0.1 molar sodium hydroxide at 25°C, the half-lives would be expected to be 23.9 days (BDNPA) and 38.7 days (BDNPF).

TABLE 1. ALKALINE HYDROLYSIS OF BDNPA/BDNPF: PRODUCT FORMATION

$$M \times 10^{-3}$$

$BDNPA_0^a$	$BDNPF_0^b$	$NaOH_0^c$	$NaOH_f^d$	NO_2^-	$CH_3C(NO_2)_2^-$	CH_3COO^-	$HCOO^-$
32.6^e	-	222.6	89.3	66.0	12.7	23.0	13.0
-	36.7^f	212.8	57.1	72.8	18.4	14.0	31.8

(a) Dioxane-water: 53/47 (v/v); 70°C; 100% hydrolysis.

(b) Dioxane-water: 53/47 (v/v); 63°C; 100% hydrolysis.

(c) Initial concentration.

(d) Final concentration.

(e) Moles NaOH reacted/Moles BMDPA reacted = 4.09.

(f) Moles NaOH reacted/Moles BDNPF reacted = 4.24.

TABLE 2. ALKALINE HYDROLYSIS OF BDNPA: FORMATION OF NITRITE AND
1,1-DINITROETHANE ANIONS AS A FUNCTION OF BASE STRENGTH AND SOLVENT

Solvent	°C	NaOH[a]	Product Mole Ratio[b]		% Hydrolysis	%Theoretical[c] Nitrogen
			NO_2^-	$CH_3C(NO_2^-)_2$		
Water[d]	70	0.2076	1.49	0.93	80.6	84
Dioxane-Water[e]	70	0.2226	2.02	0.39	100	70
Ethanol[f]	40	0.1492	2.30	0.35	98.6	75
Ethanol	55	0.1380	2.16	0.39	100	74
Ethanol	55	1.65	1.42	0.71	100	71

(a) Molarity, NaOH>>BNDPA.

(b) (Moles NO_2^- or $CH_3C(NO_2^-)_2$ formed)/(moles BDNPA reated).

(c) (2 X Product Mole Ratio $CH_2C(NO_2^-)_2$ + Product Mole Ratio NO_2^-)/4 X 100.

(d) See Table 4, run 4.

(e) Dioxane-water: 53/47 (v/v).

(f) See Table 4, run 1.

TABLE 3. ALKALINE HYDROLYSIS OF BDNPF: FORMATION OF NITRITE AND
1,1-DINITROETHANE ANIONS AS A FUNCTION OF BASE STRENGTH AND SOLVENT

Solvent	°C	NaOH[a]	Product Mole Ratio[h]		% Hydrolysis	%Theoretical[c] Nitrogen
			NO_2^-	$CH_3C(NO_2)_2^-$		
Water[d]	70	0.2180	1.29	0.86	87.0	75
Water[e]	70	0.2128	1.57	0.95	67.8	87
Dioxane-Water[f]	70	0.2257	2.02	0.59	94.0	80
Dioxane-Water	55	0.2101	2.24	0.37	92.3	75

(a) Molarity, NaOH>>BDNPF.
(b) (Moles of NO_2^- or $CH_3C(NO_2^-)_2$ formed)/(moles BDNPF reacted).
(c) (2 X Product Mole Ratio $CH_3C(NO_2)_2$ + Product Mole Ratio NO_2^-)/4 X 100.
(d) See Table 4, run 13.
(e) See Table 4, run 12.
(f) See Table 4, run 14.

TABLE 4. KINETIC DATA: RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF
BDNPA AND BDNPF

Run	Compound	Solvent	°C	NaOH[a]	Data Points	k_1[b] $\times 10^{-4}$	k_2[e]
1	BDNPA	Ethanol	40	0.1492	7	12.4 ± 1.1	83 ± 7
2	BDNPA	Water	55	0.9393	7	1.13± 0.13	1.2 ± 0.1
3	BDNPA	Water	55	1.884	7 [d]	2.9 ± 0.2	1.5 ± 0.1
4	BDNPA	Water	70	0.2076	7	1.4 ± 0.2	6.9 ± 1.1
5	BDNPA	Water	70	0.9767	8	6.6 ± 1.0	6.8 ± 1.0
6	BDNPA	Dioxane-Water[e]	70	0.2014	10[f]	12.5 ± 0.5	62.1 ± 2.7
7	BDNPF	Dioxane-Water[e]	45	0.1977	5	0.43 ± .03	2.1 ± 0.1
8	BDNPF	Water	55	0.2111	6[d]	0.33 ± .02	1.5 ± 0.1
9	BDNPF	Dioxane-Water[e]	55	0.1946	7	1.3 ± 0.1	6.5 ± 0.8
10	BDNPF	Dioxane-Water[e]	55	0.1967	6	1.1 ± 0.1	5.7 ± 0.8
11	BDNPF	Water	63	0.2111	6	0.83 ± 0.03	3.9 ± 0.1
12	BDNPF	Water	70	0.1189	7	1.3 ± 0.2	11.0 ± 1.9
13	BDNPF	Water	70	0.2128	10	1.8 ± 0.1	8.5 ± 0.3
14	BDNPF	Water	70	0.2180	7	2.3 ± 0.3	10.6 ± 1.3
15	BDNPF	Dioxane-Water[e]	70	0.2257	9	7.0 ± 0.5	31.1 ± 2.2
16	BDNPF	Dioxane-Water[e]	70	0.1961	10[g]	6.2 ± 0.4	31.5 ± 1.9

(a) Molarity, NaOH>>BDNPA or BDNPF.
(b) First order rate constant, $k_1 = t^{-1} \ln (C_0/C_t)$, sec^{-1}. Linear regression
equations for the data were calculated by a least squares method which gave
the error in the rate constant and the correlation coefficient. At the 95%
confidence level (Student's t test), correlation coefficients were better than
0.99. Errors in k_1 reflect the standard error/squared deviants value and the t
value for the data points used.
(c) Second order rate constant, $k_2 = k_1/NaOH$, $Lmole^{-1}sec^{-1}$. Errors in k_2
parallel errors in k_1.
(d) See Figure 1.
(e) Dioxane-water: 53/47 (v/v).
(f) See Table 5 and Figure 2.   (g) See Table 6 and Figure 3.

14

TABLE 5.   KINETIC DATA: ALKALINE HYDROLYSIS OF BDNPA[a]

| Time, min[b] | BDNPA[c] | M X 10^{-3} | | % Hydrolysis | Mole Ratio $NO_2^-/CH_3C(NO_2)_2^-$ |
		NO_2^-d	$CH_3C(NO_2^-)_2$[e]		
0	3.55	0	0	0	-
0.67	3.38	0.278	0.029	4.79	9.5
2.45	3.03	0.988	0.166	14.6	5.9
4.06	2.71	1.45	0.269	23.7	5.4
5.75	2.45	1.93	0.382	31.0	5.1
7.97	2.02	2.55	0.508	43.1	5.0
10.37	1.64	3.20	0.634	53.8	5.0
12.78	1.39	3.58	0.725	60.8	4.9
19.88	0.95	4.43	0.886	73.2	5.0
47.44	0.098	5.98	1.180	97.2	5.1
67.87	0	6.40	1.223	100	5.2

(a) Solvent: dioxane-water: 53/47 (v/v); NaOH = 0.2014 M; 70°C; See Table 4, run 6.

(b) Obtained with an automatic timer, Precision Scientific Co., Chicago, IL.

(c) Determined by liquid chromatography (LC).

(d) Determined by ion chromatography (IC).

(e) Determined spectrophotometrically with a Cary 16 spectrometer.

TABLE 6. KINETIC DATA: ALKALINE HYDROLYSIS OF BDNPF[a]

Time, min[b]	BDNPF[c]	NO_2^- [d]	$CH_3C(NO_2)_2^-$ [e]	% Hydrolysis	$NO_2^-/CH_3C(NO_2)_2^-$
		M X 10^{-3}			Mole Ratio
0	3.67	0	0	0	-
0.56	3.57	0.189	0.005	2.72	-
2.90	3.08	0.890	0.277	16.1	3.2
5.01	2.70	1.41	0.452	26.4	3.1
6.50	2.57	1.64	0.566	30.0	2.9
8.03	2.38	1.75	0.659	35.1	2.7
9.87	2.22	2.01	0.763	39.5	2.6
11.52	2.12	2.20	0.863	42.2	2.5
19.48	1.61	2.88	1.205	56.1	2.4
30.77	1.13	3.56	1.565	69.2	2.3
51.97	0.48	4.60	1.870	86.9	2.5

(a) Solvent: Dioxane-water: 53/47 (v/v); NaOH = 0.1961 M; 70°C; see Table 4, run 16.

(b) Obtained with an automatic timer, Precision Scientific Co. Chicago, ILL.

(c) Determined by liquid chromatography (LC).

(d) Determined by ion chromatography (IC).

(e) Determined spectrophotometrically with a Cary 16 spectrometer.

TABLE 7. ALKALINE HYDROLYSIS OF BDNPA/BDNPF: ACTIVATION PARAMETERS[a]

Compound	Solvent	$\Delta H^{\neq b}$	$\Delta F^{\neq b,g}$	$\Delta S^{\neq c,h}$
BDNPA	Water	23.9[d]	25.1	-3.5
BDNPF	Water	27.3[e]	25.0	+7.0
BDNPF	Dioxane-water	22.8[f]	24.1	-3.9

(a) Calculated from data given in Table 4.

(b) Kcal/mole, at 55°C.

(c) Cal/deg at 55°C.

(d) Calculated from slope of ln k_2 versus 1/T for values of k_2 at 55 and 70°C. from the expression, $\Delta H^{\neq} = (slope \times R) - RT$

(e) Correlation coefficient was 0.998 for the linear regression equation of a plot of ln k_2 versus 1/T, with an error of ± 4.9%, Figure 4.

(f) Correlation coefficient was 0.999 for the linear regression equation of a plot of ln k_2 versus 1/T, with an error of ± 2.1%, Figure 4.

(g) Calculated from the expression, $\Delta F^{\neq} = -RT \ln (k_2 h/kT)$, where k_2 is the second order rate constant; h is Planck's constant; k is Boltzmann's constant and T is the absolute temperature.

(h) Calculated from the expression, $\Delta S^{\neq} = (\Delta H^{\neq} - \Delta F^{\neq})/T$.

TABLE 8. RELATIVE RATES OF ALKALINE HYDROLYSIS OF SEVERAL CLASSES OF
ENERGETIC COMPOUNDS IN WATER AT 55°C

Class	Compound	$k_2{}^a \times 10^{-4}$	Relative Rate
Nitrate ester	TEGDN	0.036^b	1.0
Nitrate ester	MTN	0.13^c	3.6
Geminal dinitro acetal	BDNPA	1.4^d	39
Geminal dinitro formal	BDNPF	1.5^d	41
Nitramine	RDX[e]	1500	42,000

(a) Second order rate constant in water at 55°C, $Lmole^{-1}sec^{-1}$.

(b) Reference 2.

(c) Reference 1.

(d) This study.

(e) Reference 3.

FIGURE 1. ALKALINE HYDROLYSIS OF BDNPA/BDNPF IN WATER AT 55° C
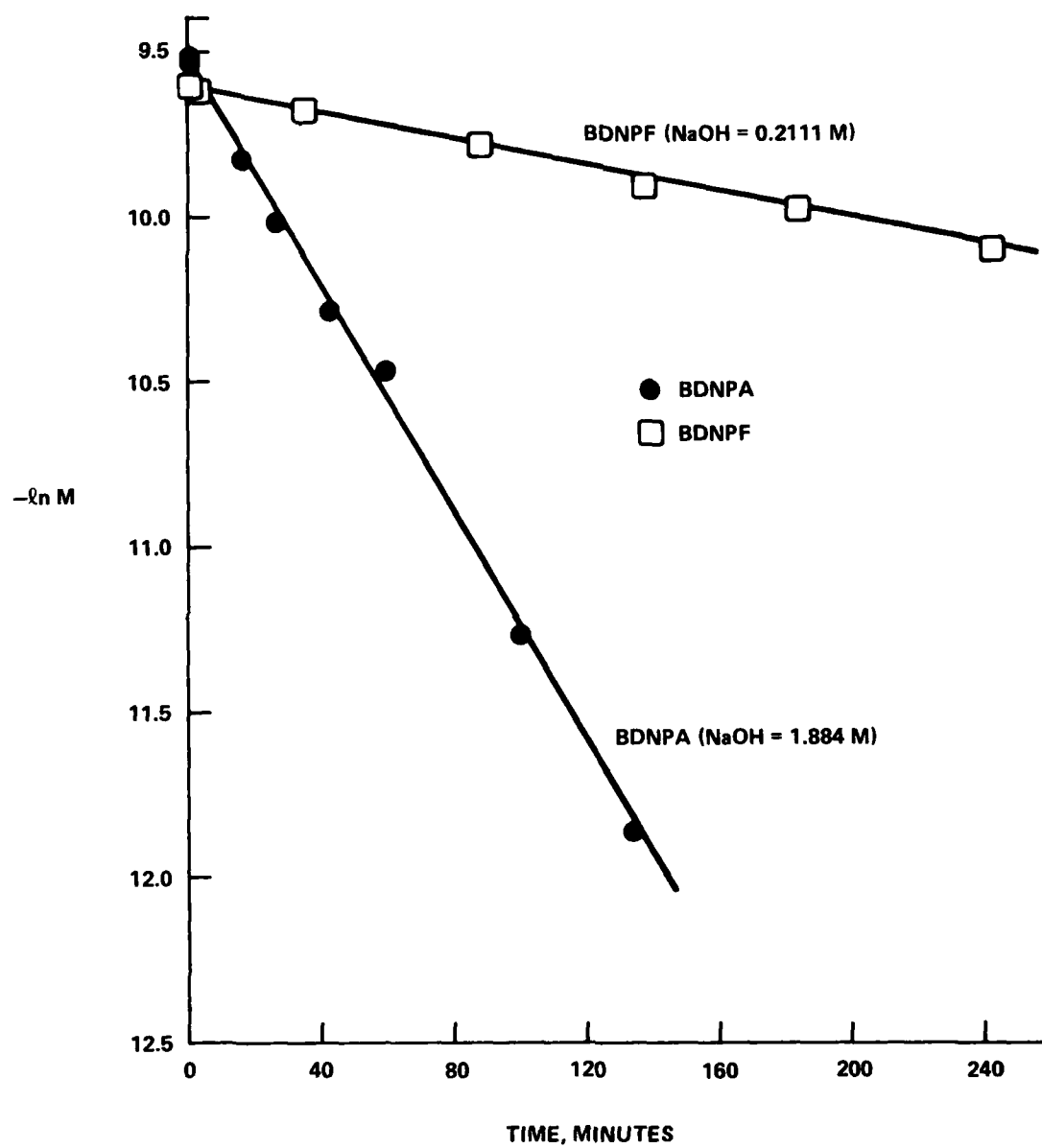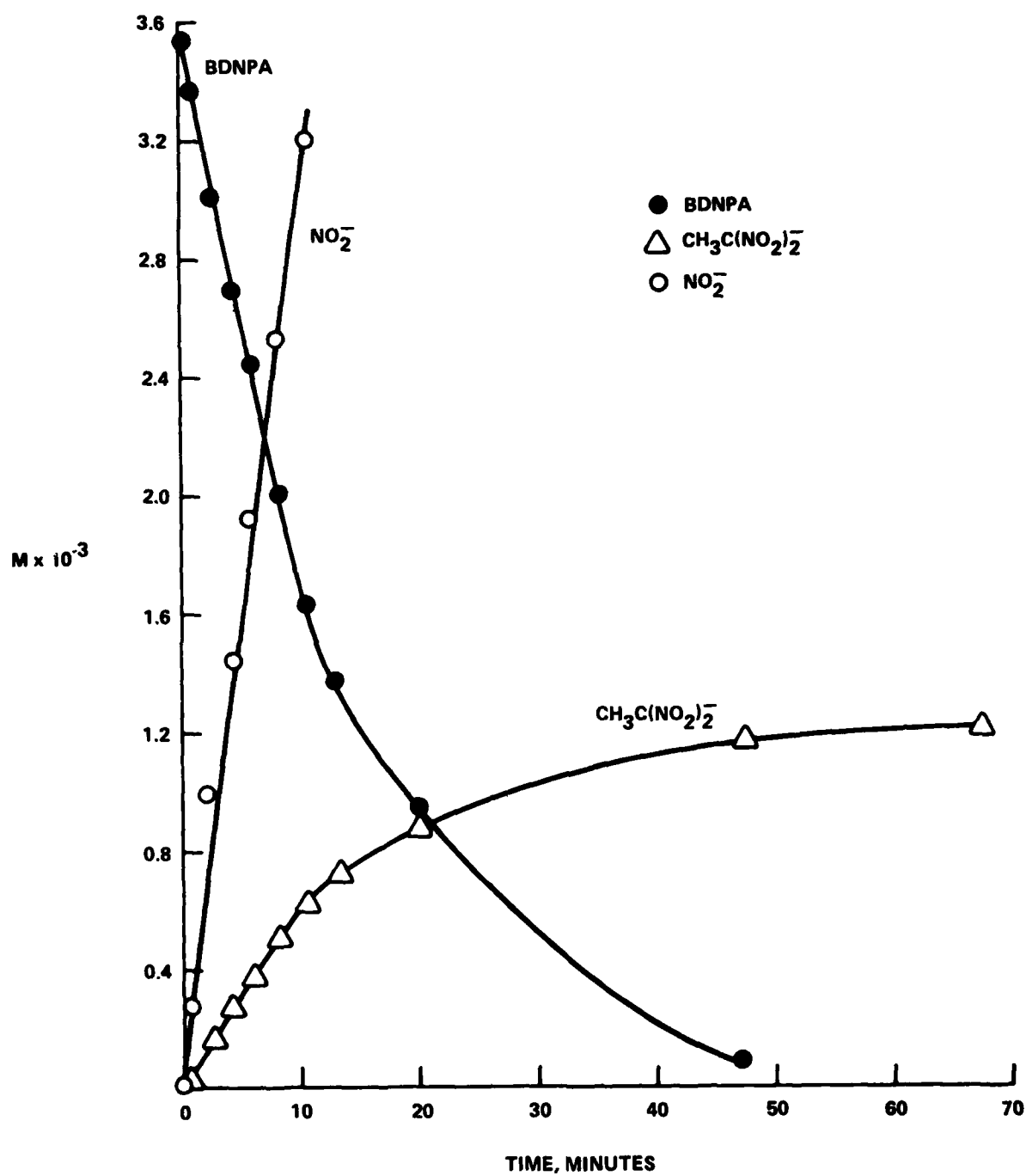(ℓ n CONCENTRATION VERSUS TIME)

FIGURE 2. ALKALINE HYDROLYSIS OF BDNPA: FORMATION OF NITRITE AND
1,1-DINITROETHANE ANIONS (CONCENTRATION VERSUS TIME)
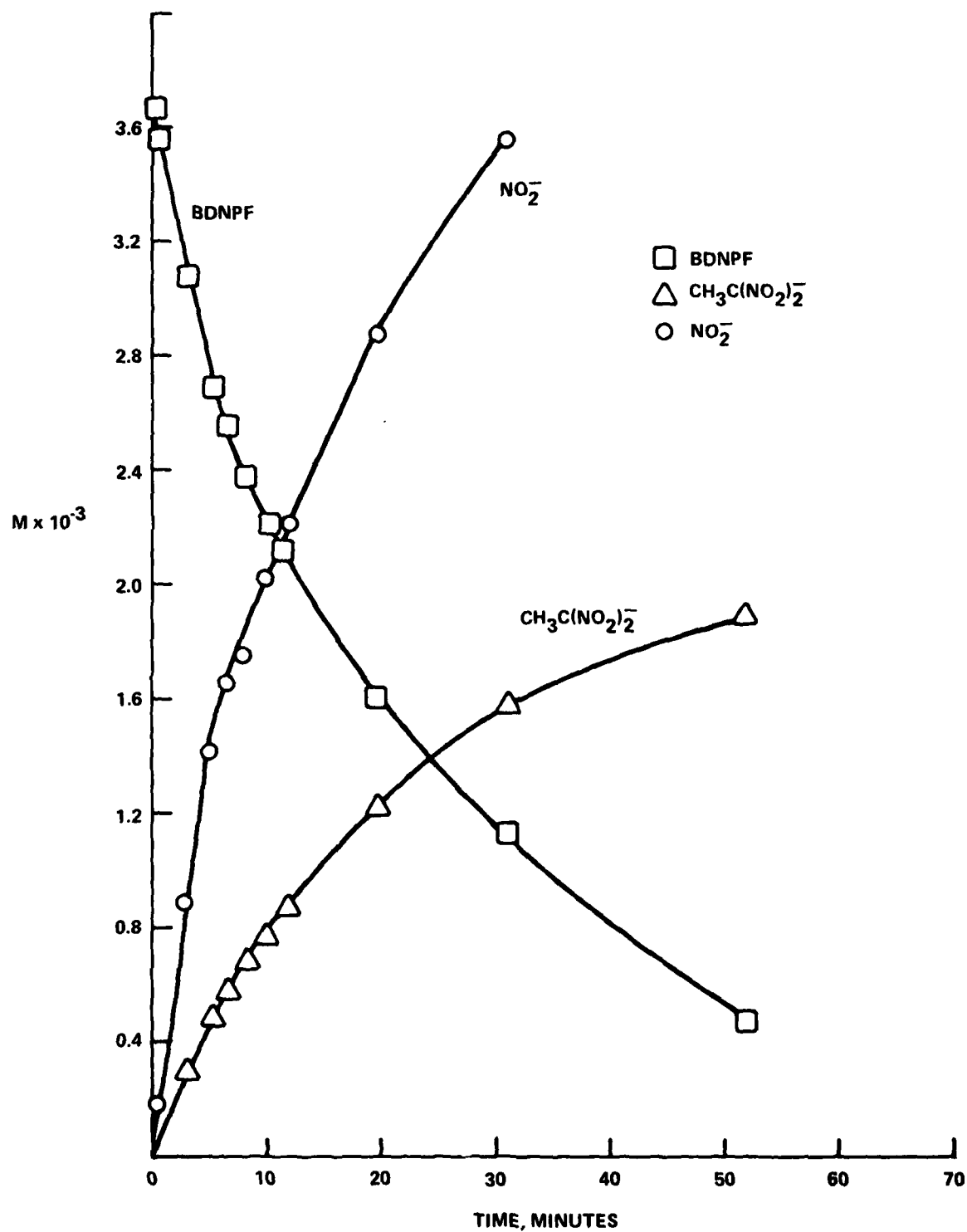
FIGURE 3. ALKALINE HYDROLYSIS OF BDNPF: FORMATION OF NITRITE AND
1,1-DINITROETHANE ANIONS (CONCENTRATION VERSUS TIME)
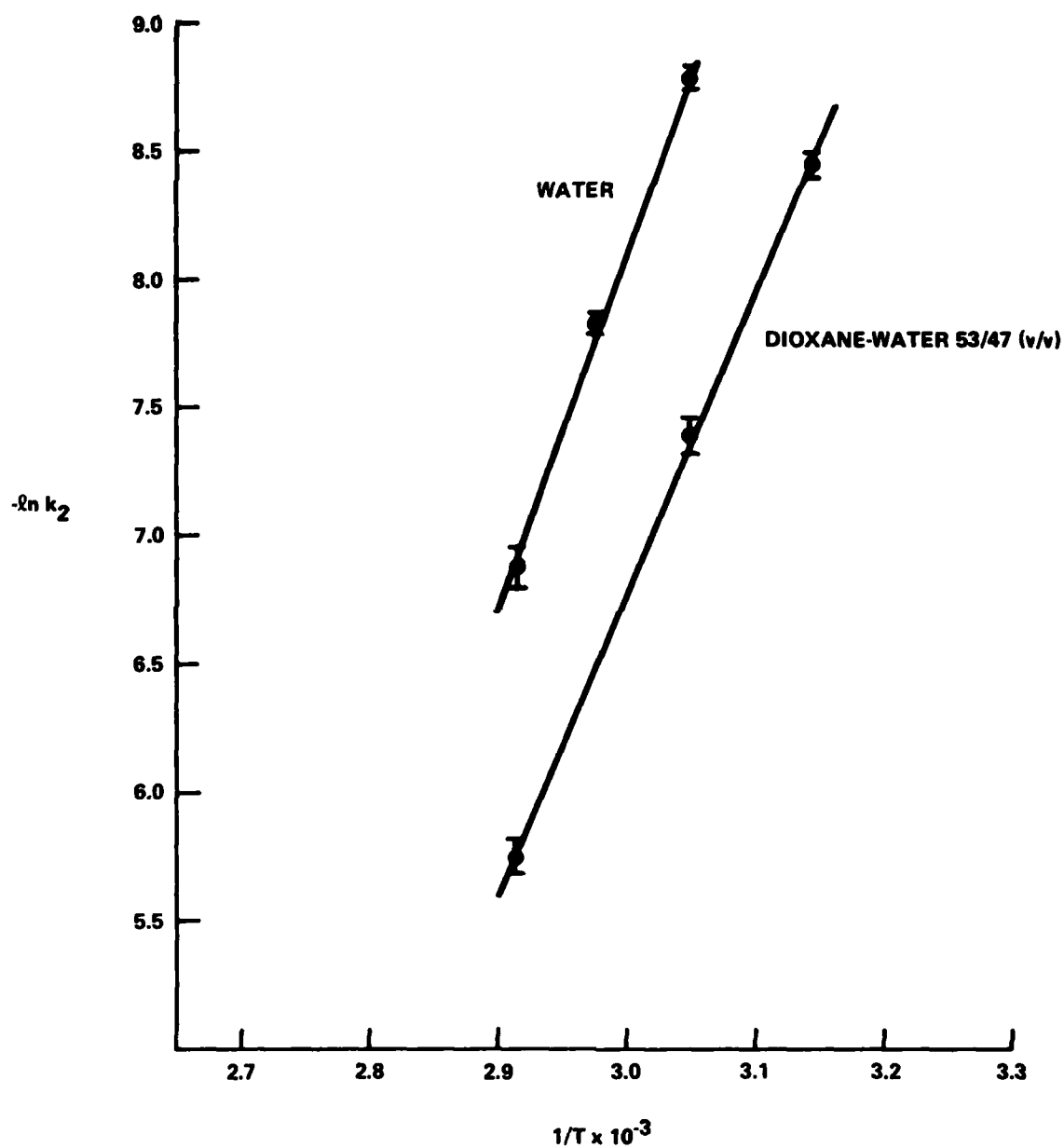
FIGURE 4. ALKALINE HYDROLYSIS OF BDNPF IN WATER AND DIOXANE-WATER ($-\ln k_2$ VERSUS $1/T$)

DISTRIBUTION

	Copies		Copies
Chief of Naval Material		Commander	
Attn: MAT 08T2	1	Naval Electronic Systems Command	
MAT 08L	1	Attn: ELEX-03A	1
Department of the Navy		ELEX-9053	1
Washington, DC 20360		Naval Electronic Systems Command Headquarters Washington, DC 20360	
Chief of Naval Operations			
Attn: NOP-411	1		
NOP-411F	1	Commander	
NOP-621C	1	Naval Facilities Engineering	
Department of the Navy		Command	
Washington, DC 20350		Attn: 032E	1
		Attn: 09M22C	1
Chief of Naval Research		200 Stovall Street	
Attn: ONR-102	1	Alexandria, VA 22332	
ONR-420	1		
ONR-460	1	Commander	
ONR-463	1	Naval Sea Systems Command	
ONR-465	1	Attn: SEA-04H	1
OMR-474	1	SEA-04H11	1
800 North Quincy St.		SEA-04H12	1
Arlington, VA 22217		SEA-04H13	1
		SEA-55X13	1
Commander		(D. Lund)	1
Naval Air Systems Command		(W. Forehand)	1
Attn: AIR-03B	1	SEA-62R32 (G. Edwards)	1
AIR-03C	1	SEA-62R31 (R. Bailey)	1
AIR-09E3	1	SEA-064E (R. Beauregard)	1
AIR-350 (H. Benefiel)	1	SEA-00612	1
AIR-541	1	Naval Sea Systems Command	
AIR-541A	1	Headquarters	
AIR-5411	3	Washington, DC 20362	
AIR-5413	1		
AIR-950D	1		
Naval Air Systems Command Headquarters			
Washington, DC 20361		Commander	
		Naval Weapons Center	
Officer-in-Charge		Attn: Library	1
Civil Engineering Laboratory		A. Amster	1
Attn: L31	1	W. Froehner	1
L. Huang	1	K. Graham	1
W. Keenan	1	T. Joyner	1
J. Tancreto	1	J. Kinney	1
Naval Construction Battalion		D. Kumferman	1
Center		D. Lind	1
Port Hueneme, CA 93043		H. Mallory	1
		J. Pakulak	1
		R. Sewell	1
		E. Erickson	1
		China Lake, CA 93555	

DISTRIBUTION (Continued)

	Copies		Copies
Commanding Officer Naval Research Laboratory Attn: Technical Information Section Washington, DC 20375	1	Superintendent Naval Postgraduate School Attn: Library Monterey, CA 93940	1
Commander David W. Taylor Naval Ship R & D Center		President Naval War College Newport, RI 02840	1
Attn: Library	1		
F. Fisch	1		
O. Hackett	1		
G. Remmars	1	Commander	
J. Sykes	1	Naval Air Development Center	
S-L Wang	1	Attn: G. Duval	1
F. Weinberger	1	Warminister, PA 18974	
B. Whang	1		
Bethesda, MD 20084			
		Commanding Officer	
Naval Ship Research and Development Center		Naval Air Engineering Center Lakehurst, NJ 98733	1
Attn: Library	1		
R. Walker	1		
Underwater Explosions Research Division Portsmouth, VA 23709		Commanding Officer Naval Coastal Systems Center Attn: Tech Library Panama City, FL 32407	1
Superintendent U. S. Naval Academy Annapolis, MD 21402	1	Officer-in-Charge Naval Mine Engineering Facility Yorktown, VA 23691	1
Commanding Officer Naval Explosive Ordnance Disposal Facility Attn: Technical Library Indian Head, MD 20640	1	Commanding Officer Naval Underwater System Center Newport, RI 02840	
		Commanding Officer Naval Weapons Station Charleston, SC 29408	1
Commander Naval Ocean Systems Center San Diego, CA 92152	1	Commanding Officer Naval Weapons Station Colts Neck, NJ 07722	1
Commanding Officer Naval Ordnance Missile Test Facility White Sands Missile Range,NM 88002	1	Commanding Officer Naval Weapons Station Concord, CA 94520	1

DISTRIBUTION (Continued)

Copies   Copies

Commanding Officer Naval Ordnance Station Attn: Technical Library Indian Head, MD 20640	1	Commanding Officer Naval Weapons Station Seal Beach, CA 90740	1
Commanding Officer Naval Ordnance Station Louisville, KY 40214	1	Commanding Officer Naval Weapons Station Research and Development Div. Attn: W. McBride Yorktown, VA 23691	1
Commander Naval Safety Center Naval Air Station Norfolk, VA 23511	1	Commanding Officer Naval Weapons Support Center Crane, IN 47522	1
Commanding Officer Naval Ship Weapons Systems Engineering Station Port Hueneme, CA 93043	1	Commander Pacific Missile Test Center Point Mugu, CA 930421	1

Commanding Officer
Naval Undersea Warfare
    Engineering Station
Keyport, WA 98345
	1	Director
		Strategic Systems Project Office
		Attn: SP-27
		      OP-2701
		Department of the Navy
		Washington, DC 20376
			1
			1

Commandant of the Marine Corps
Attn: MC-OTOO
    MC-LMW-50
Navy Department
Washington, DC
	1
	1
		Commanding General
		U. S. Army Engineer Center
		Attn: Assist. Commandant
		      Engineering School
		Fort Belvoir, VA 22060
			1

Commanding Officer U. S. Army Combat Dev. Comm. Fort Belvoir, VA 22060	1	Director U. S. Army Material Command Field Safety Activity Attn: Library Charlestown, IN 47111	1

Commanding Officer
U. S. Army Material, Development
  and Readiness Research Comm.
Attn: Technical Library
    DRCDE
    DRCSF
5001 Eisenhower Avenue
Alexandria, VA 22333
	1
	1
	1
		Commanding Officer
		Aberdeen Research and Development
		  Development Center
		Attn: Technical library
		      R. Frye
		      P. Howe
		      J. Keefer
		      C. Kingery
		      J. Roccio
		      R. Shear
		      J. Sperrazza
		Aberdeen, MD 21005
			1
			1
			1
			1
			1
			1
			1

Headquarters U. S. Army Munition Command Attn: Library Dover, NJ 07801	1		

DISTRIBUTION (Continued)

	Copies		Copies

Chief of Engineers
Attn: DAEN-ASI-L   1   Commanding Officer
      DAEN-RDZ-A   1   U. S. Army Armament Research
      DAEN-SQZ-A   1   and Development Command
Department of the Army   Attn: DRDAR-LCE-M   1
Washington, DC 20314   Technical Library   1
                                               J. Hershkowitz   1
Director   N. Slagg   1
U. S. Army Engineer Waterways   R. Walker   1
   Experiment Station   Dover, NJ 07801
Attn: Library   1
      D. Day   1   Commanding Officer
      L. Ingram   1   U. S. Army Cold Regions Research
      D. Murrell   1   and Engineering Laboratories
      A. Rooke   Attn: Library   1
P. O. Box 63   M. Mellor   1
Vicksburg, MS 39180   Hanover, NH 03755

Commander
U. S. Army Medical Bioengineering   OOAMA
R & D Laboratory   Hill AFB
Attn: W. D. Burrows   1   Attn: MME   1
      K. F. Kenyon   1   Ogden, UT 84401
Fort Detrick, MD 21701

Commanding General   Commander
U. S. Army Natick Research and   Air Force Weapons Laboratory
   Development Command   Kirtland Air Force Base
Attn: Library   1   Albuquerque, NM 87117   1
      D. Sieling   1
Natick, MA 01762
                                         Commander
Commander   Armament Development and Test Center
Harry Diamond Laboratories   Attn: DLOSL   1
Attn: Technical Library   1   DLW   1
2800 Powder Mill Rd   Eglin AFB, FL 32542
Adelphi, MD 20783
                                         Air Force Cambridge Research
Commandant   Laboratories
U.S. Army Engineer School   L. G. Hanscom Field
Attn: ATSE-CDC   1   Attn: Library   1
       ATSE-DTE-ADM   1   Bedford, MA 01730
Fort Belvoir,VA 22060
                                         Air University Library
Commandant   Attn: Documents Section   1
Army War College   Maxwell, AFB, AL 26112
Attn: Library   1
Carlisle Barracks, PA 17013

DISTRIBUTION (Continued)

	Copies		Copies
Commandant Industrial College of the Armed Forces Fort Leslie J. McNair Attn: Document Control Washington, DC 20315	1	Air Force Logistics Command Wright-Patterson AFB Attn: A. E. Adams Ohio 45433	1
Commandant National War College Fort Leslie J. McNair Attn: Class, Rec Library Washington, DC 20315	1	Library of Congress Attn: Gift and Exchange Division Washington, DC 20540	4
Headquarters Air Force Systems Command Andrews AFB Attn: Technical Library Washington, DC 20331	1	Defense Technical Information Center Cameron Station Alexandria, VA 22314	12
		Director of Defense Research and Engineering Attn: Tech. Library Washington, DC 20330	1

Chairman
Department of Defense
   Explosives Safety Board
Attn: DDESB-KT
      P. Price
      T. Zaker
Room 856-C, Hoffman Bldg
2461 Eisenhower Ave
Alexandria, VA 22331
	1
	1
	1
	1
		Kaman-Tempo
		Attn: JK. Petes
		2560 Huntington Ave.
		Alexandria, VA 22303
			1

		Hercules, Inc. Attn: D. Richardson Box 98 Magna, UT 84044	1

Director
Advanced Research Projects
   Projects Agency
Attn: Library
Washington, DC 20301
	1	IIT Research Institute
		Attn: Technical Library
		      J. Dahn
		      H. Napadensky
		10 West 35th St.
		Chicago, IL 60616
			1
			1
			1

Director
Defense Nuclear Agency
Attn: Technical Library
      SPAS
      SPSS
      SPTD
Washington, DC 20305
	1
	1
	1
	1
		Institute for Defense Analysis
		Attn: Library
		400 Army-Navy Drive
		Arlington, VA 22202
			1

DISTRIBUTION (Continued)

	Copies		Copies
Commander Field Command Defense Nuclear Agency Attn: FCTOH Kirtland AFB, NM 87115	1	Kaman Sciences Corporation Post Office Box 7463 Colorado Springs, CO 80907	1
Battelle Memorial Institute 505 King Avenue Columbus, OH 43201	1	Los Alamos National Laboratory Attn: LASL Library C. Mader R. Rogers L. Smith S. Yasuda Post Office Box 1663 Los Alamos, NM 87544	1 1 1 1 1
Denver Research Institute Mechanical Sciences and Environmental Engineering University of Denver Attn: J. Wisotski Denver, CO 80210	1		
Physics International Attn: F. Saber 2700 Merced Street San Leandro, CA 94577	1	New Mexico Institute of Mining and Technology TERA Attn: M. L. Kempton J. P. McLain Socorro, NM 87801	1 1
Pittsburg Mining and Safety Research Center U. S. Bureau of Mines Attn: R. Vandolah R. Watson 4800 Forbes Avenue Pittsburg, PA 15213	1 1 1	Pacifica Technology Post Office Box 148 Del Mar, CA 92014	1
		University of New Mexico Eric H. Wang Civil Engineering Facility University Station Box 188 Albuquerque, NM 87131	1
Sandia National Laboratories Attn: Library J. Reed L. Vortman Post Office Box 5800 Albuquerque, NM 87115	1 1 1 1	Lovelace Foundation for Medical Education 5200 Gibson Blvd, Southeast Albuquerque, NM 87108	1
Southwest Research Insitutute Attn: W. Baker J. Hokanson 8500 Culebra Road San Antonio, TX 78206	1 1	Commander Submarine Group 5 Attn: LCDR Duchesneau San Diego, CA 92132	1
University of California Lawrence Livermore National Laboratory Attn: M. Finger E. James E. Lee Post Office Box 808 Livermore, CA 94550	1 1 1 1	Commander Submarines Pacific Attn: 22 San Francisco, CA 96610	1

DISTRIBUTION (Continued)

Copies

URS Corporation
Attn: Document Control   1
155 Bonet Road
San Mateo, CA 94550

Internal Distribution:
E431		9
E432		3
E35		1
X432		1
R11	(H. G. Adolph)	1
	(D. A. Cichra)	1
	(G. W. Lawrence)	1
	(M. J. Kamlet)	1
	(W. M. Koppes)	1
	(J. F. Leahy)	1
	(T. N. Hall)	1
	(M. E. Sitzmann)	1
	(T. Adams)	1
	(M. E. Chaykovsky)	1
R10	(K. F. Mueller)	1
R14	(G. A. Young)	1
R16	(M. Sidorowicz)	1
	(D. J. Glover)	5
	(J. C. Hoffsommer)	10
	(E. G. Kayser)	1
	(H. S. Haiss)	1
	(A. S. Tompa)	1
	(G. B. Wilmot)	1
	(R. A. Robb)	1
	(R. H. Renner)	1
	(J. E. Mastroianni)	1
	(J. S. Deiter)	1
	(J. A. Glatz)	1
	(L. A. Lee)	1
	(A. C. Richardson)	1
	(J. P. Consaga)	1
	(W. F. Bryant)	1